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# SENSITIVITY OF THE LASER EMISSION SPECTROGRAPHY METHOD IN THE ANALYSIS OF NONCONDUCTIVE POWDER SAMPLES

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# SENSITIVITY OF THE LASER EMISSION SPECTROGRAPHY METHOD IN THE ANALYSIS OF NONCONDUCTIVE POWDER SAMPLES*

by

Tsuneko Yamane and Sumeo Matsushita**

## 1. Introduction

Ever since laser light started to be used for evaporating and volatilizing samples for emission spectrography [1-4], there have been developments of laser emission spectrography on account of the following characteristic features. First, minute parts can be analyzed with a high sensitivity [5-10]. Second, even nonconductive samples can be evaporated in unmodified form in the same manner as conductive samples.

This report deals with the sensitivity of detection of nonconductive powder samples in laser emission spectrography. After the powder samples were mixed with phenol resin and were heat cured, they were excited by a two-stage method combining laser light obtained by normal pulse oscillation with spark discharge obtained with a carbon auxiliary electrode.

In a previous report [10], the authors have already reported the sensitivity for magnesium, beryllium, and calcium at x $10^{-14}$ g (x $10^{-5}$%), and for manganese, copper, silver, and strontium at x $10^{-13}$ g (x $10^{-4}$%).

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## 2. The Experiments

### 2.1 Apparatus

Laser apparatus: LMA-1 manufactured by VEB Carl Zeiss, Jena [11]. Normal pulse oscillation by means of neodymium-glass lasers. Maximum output 1 $W_s$. Two-stage excitation method adopting also spark discharge by means of carbon auxiliary electrode. The objective for condensing the lasers was a 40 x /0.5 catoptric lens.

Spectroscope: Medium size crystal spectroscope Q-24 manufactured by VEB Carl Zeiss, Jena. The slit image-formation method, using a UV achromatic condenser lens, was employed.

Photographic plates: Fuji HS plates. Developing was D-19, 20° C, 5 minutes.

Photometry: Used a microphotometer manufactured by R. Fuess.

### 2.2 Samples

Spex Mix (No. 1000) was used as the nonconductive powder samples, as in the previous report [10]. Each sample was diluted to a definite concentration by means of RW-A graphite powder manufactured by Ringsdorff Werke, and was mixed using Wig-L-Bug (Spex). This powder was mixed evenly with a phenol resin specially refined for emission spectrography at a weight ratio of 1:1. This mixed powder was laid on a carbon plate and heated extremely slowly in an electric furnace. It was used after it had been kept at 150° C for three hours and heat cured. The size of the samples subjected to the experiments was 15 x 5 x 5 mm.

2.3 Experimental Methods

Thin slices were cut off the surface of the samples, and the flat parts were irradiated with one shot of laser light. The experimental conditions were selected so that there would be a crater diameter of 100μ and the depth would be one-half of the diameter (amount of consumption $10^{-7}$ g). In selecting the gap between electrodes and the gap between the sample and the electrodes, the results already reported [10] were taken into account. The amount of consumption was calculated approximately from the volume of the crater. The experimental conditions are shown in Table I.

Table I Experimental parameters

| | |
|---|---|
| Flash lamp voltage | : 1.2 kV |
| Objective | : 40×/0.5 Catoptric lens system |
| Electrodes gap | : 800 μ |
| Position of electrodes | : 1000 μ above sample |
| Spark excitation | : 2.6 kV, 2.5 μF, 125 μH, 100 discharges per sec. |
| Crater diameter | : 100 μ |
| Slit width | : 15 μ |
| Photographic plates | : Fuji HS (FBO) |

As for the sensitivity of detection, as was already reported [10], the intensity of the analytical beams was obviously stronger than their backgrounds at each concentration. If the blackness of the analytical beam and that of its position when it was a blank are $S_L$ + U and $S_U$ respectively, then the results quite thoroughly satisfied $S_{L+U} > S_U + 3\sigma$ ($\sigma$ is the standard deviation in the difference between the blackness of $S_U$ and that of the background in its vicinity).

## 3. Results and Considerations

The sensitivity of detection is shown in Table II. The data here for magnesium, beryllium, calcium, manganese, copper, silver, and strontium were quoted from the previous report [10]. The experimental conditions for

these elements were the same as in Table I.

Table II Sensitivity of non-conductive powder

| Element | Spectral line (Å) | Approximate sensitivity | |
|---|---|---|---|
| | | Relative (%) | Absolute (g) |
| Mg† II | 2795.53 | $\times 10^{-5}$ | $\times 10^{-14}$ |
| Be† II | 3130.416 | $\times 10^{-5}$ | $\times 10^{-14}$ |
| Ca† II | 3933.666 | $\times 10^{-5}$ | $\times 10^{-14}$ |
| Mn† II | 2576.104 | $\times 10^{-4}$ | $\times 10^{-13}$ |
| Cu† I | 3247.540 | $\times 10^{-4}$ | $\times 10^{-13}$ |
| Ag† I | 3280.683 | $\times 10^{-4}$ | $\times 10^{-13}$ |
| Sr† II | 4077.714 | $\times 10^{-4}$ | $\times 10^{-13}$ |
| B I | 2497.733 | $\times 10^{-3}$ | $\times 10^{-12}$ |
| Cd I | 2288.018 | $\times 10^{-3}$ | $\times 10^{-12}$ |
| V II | 3102.299 | $\times 10^{-3}$ | $\times 10^{-12}$ |
| Fe II | 2395.625 | $\times 10^{-3}$ | $\times 10^{-12}$ |
| Cr II | 2843.252 | $\times 10^{-3}$ | $\times 10^{-12}$ |
| Zr II | 3391.975 | $\times 10^{-3}$ | $\times 10^{-12}$ |
| Sn I | 3175.019 | $\times 10^{-3}$ | $\times 10^{-11}$ |
| Bi I | 3067.716 | $\times 10^{-2}$ | $\times 10^{-11}$ |
| Mo II | 2816.154 | $\times 10^{-2}$ | $\times 10^{-11}$ |
| Ti II | 3349.035 | $\times 10^{-2}$ | $\times 10^{-11}$ |
| Zn I | 3345.020 | $\times 10^{-2}$ | $\times 10^{-11}$ |
| Co I | 3453.505 | $\times 10^{-2}$ | $\times 10^{-11}$ |
| Al I | 3082.155 | $\times 10^{-2}$ | $\times 10^{-11}$ |
| Ni I | 3414.765 | $\times 10^{-2}$ | $\times 10^{-11}$ |
| Pb I | 2833.069 | $\times 10^{-1}$ | $\times 10^{-10}$ |

† T. Yamane, S. Suzuki, S. Matsushita : *Bunko Kenkyu*, **18**, 147 (1970)

Since Spex Mix was used as the powder sample, there were many disturbing beams, and for this reason it was not possible to measure the sensitivity for all the elements contained in the samples which are capable of being analyzed by emission spectrography in the atmosphere. This phenomenon was observed also in the elements listed in Table II. Consequently, if it were assumed that the relevant disturbing elements had been eliminated when preparing the samples for measuring the sensitivity, it is thought that different results would be obtained for the spectral lines used and for the sensitivity of detection.

The same experiments were carried out using ZU-2 photographic plates made by ORWO (East Germany), but almost the same results as those in Table II were obtained.

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147404s Sensitivity of laser-microspectrochemical method for nonconductive powders. Yamane, Tsuneko; Matsushita, Sumeo (Dep. Inorg. Chem., Tokyo Metrop. Ind. Tech. Cent., Tokyo, Japan). *Bunseki Kagaku* 1971, 20(9), 1202-4 (Japan). Std. samples (15 × 5 × 5 mm) were prepd. by heating (150°, 3 hr) mixts. of Spex Mix No. 1000, graphite powder and phenolic resin. A laser beam from a Nd-doped glass laser was focussed on the sample and the vapor produced was then excited by an auxiliary spark discharge. A slit image method was used for slit illumination. Abs. sensitivities for the anal. lines are: Mg II 2795.53, $10^{-11}$; Be II 3130.416, $10^{-11}$; Ca II 3933.666, $10^{-14}$; Mn II 2576.104, $10^{-12}$; Cu I 3247.540, $10^{-13}$; Ag I 3280.683, $10^{-13}$; Sr II 4077.714, $10^{-12}$; B I 2497.733, $10^{-12}$, Cd I 2288.018, $10^{-12}$; V II 3102.299, $10^{-12}$; Fe II 2395.625, $10^{-12}$; Cr II 2843.252, $10^{-12}$; Zr II 3391.975, $10^{-12}$; Sn I 3175.019, $10^{-11}$; Bi I 3067.716, $10^{-11}$; Mo II 2816.154 $10^{-11}$; Ti II 3349.035, $10^{-11}$; Zn I 3345.020, $10^{-11}$; Co I 3453.505, $10^{-11}$; Al I 3082.155, $10^{-11}$; Ni I 3414.765, $10^{-11}$; Pb I 2833.069Å, $10^{-10}$ g.